

RECEIVED
CENTRAL FAX CENTER

JAN 09 2006

FAX TRANSMISSION

DATE: January 9, 2006

PTO IDENTIFIER: Application Number 10/808266-Conf. #4785
Patent Number

Inventor: Teddy M Keller et al.

MESSAGE TO: US Patent and Trademark Office

FAX NUMBER: (571) 273-8300

FROM: US NAVAL RESEARCH LABORATORY
Joseph T. Grunkemeyer

PHONE: (202) 404-1556

Attorney Dkt. #: 96202US1

PAGES (Including Cover Sheet): 27

CONTENTS: Certificate of Transmission (1 page)
Fee Transmittal (1 page)
Appeal Brief Transmittal (1 page)
Appeal Brief (23)
Charge \$500.00 to deposit account 50-0281

If your receipt of this transmission is in error, please notify this firm immediately by collect call to sender at (202) 404-1556 and send the original transmission to us by return mail at the address below.

This transmission is intended for the sole use of the individual and entity to whom it is addressed, and may contain information that is privileged, confidential and exempt from disclosure under applicable law. You are hereby notified that any dissemination, distribution or duplication of this transmission by someone other than the intended addressee or its designated agent is strictly prohibited.

US NAVAL RESEARCH LABORATORY
4555 Overlook Ave, SW, Washington, DC 20375
Telephone: (202) 767-3427 Facsimile: (202) 404-7380

BEST AVAILABLE COPY

PTO/SB/97 (09-04)

Approved for use through 07/31/2006. OMB 0651-0031

U. S. Patent and Trademark Office; U.S. DEPARTMENT OF COMMERCE

Under the Paperwork Reduction Act of 1995, no persons are required to respond to a collection of information unless it displays a valid OMB control number.

Application No. (if known): 10/808266

Attorney Docket No.: 96202US1

Certificate of Transmission under 37 CFR 1.8

I hereby certify that this correspondence is being facsimile transmitted to the United States Patent and Trademark Office.

on January 9, 2006
Date



Signature

Joseph T. Grunkemeyer

Typed or printed name of person signing Certificate

46,746

Registration Number, if applicable

(202) 404-1556

Telephone Number

Note: Each paper must have its own certificate of transmission, or this certificate must identify each submitted paper.

Fee Transmittal (1 page)

Appeal Brief Transmittal (1 page)

Appeal Brief (23)

Charge \$500.00 to deposit account 50-0281

RECEIVED
CENTRAL FAX CENTER

JAN 09 2006

PTO/SB/17 (12-04v2)
Approved for use through 7/31/2006. OMB 0651-0032
U.S. Patent and Trademark Office; U.S. DEPARTMENT OF COMMERCE

Under the Paperwork Reduction Act of 1995, no person is required to respond to a collection of information unless it displays a valid OMB control number.

Effective on 12/08/2004. Fees pursuant to the Consolidated Appropriations Act, 2005 (H.R. 4818). FEE TRANSMITTAL For FY 2005		Complete If Known	
<input type="checkbox"/> Applicant claims small entity status. See 37 CFR 1.27		Application Number	10/808266-Conf. #4785
		Filing Date	March 17, 2004
		First Named Inventor	Teddy M Keller
		Examiner Name	D. Truong
		Art Unit	1711
		Attorney Docket No.	96202US1
TOTAL AMOUNT OF PAYMENT			
(\$)		500.00	

METHOD OF PAYMENT (check all that apply)

☐ Check ☐ Credit Card ☐ Money Order ☐ None ☐ Other (please identify): _____
☒ Deposit Account Deposit Account Number: 50-0281 Deposit Account Name: US Naval Research Laboratory
 For the above-identified deposit account, the Director is hereby authorized to: (check all that apply)
☒ Charge fee(s) indicated below ☐ Charge fee(s) indicated below, except for the filing fee
☒ Charge any additional fee(s) or underpayment of fee(s) under 37 CFR 1.16 and 1.17 ☒ Credit any overpayments

FEE CALCULATION

1. BASIC FILING, SEARCH, AND EXAMINATION FEES

Application Type	FILING FEES		SEARCH FEES		EXAMINATION FEES		Fees Paid (\$)
	Fee (\$)	Small Entity Fee (\$)	Fee (\$)	Small Entity Fee (\$)	Fee (\$)	Small Entity Fee (\$)	
Utility	300	150	500	250	200	100	
Design	200	100	100	50	130	65	
Plant	200	100	300	150	160	80	
Reissue	300	150	500	250	600	300	
Provisional	200	100	0	0	0	0	

2. EXCESS CLAIM FEES

Fee Description	Fee (\$)	Small Entity Fee (\$)
Each claim over 20 (including Reissues)	50	25
Each independent claim over 3 (including Reissues)	200	100
Multiple dependent claims	360	180

Total Claims Extra Claims Fee (\$) Fee Paid (\$)
 _____ _____ _____ _____

Multiple Dependent Claims
Fee (\$) Fee Paid (\$)
 _____ _____

Indep. Claims Extra Claims Fee (\$) Fee Paid (\$)
 _____ _____ _____ _____

3. APPLICATION SIZE FEE

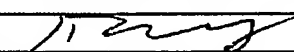
If the specification and drawings exceed 100 sheets of paper (excluding electronically filed sequence or computer listings under 37 CFR 1.52(e)), the application size fee due is \$250 (\$125 for small entity) for each additional 50 sheets or fraction thereof. See 35 U.S.C. 41(a)(1)(G) and 37 CFR 1.16(s).

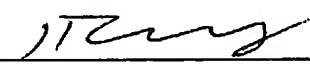
Total Sheets Extra Sheets Number of each additional 50 or fraction thereof Fee (\$) Fee Paid (\$)
 _____ _____ _____ _____ _____

4. OTHER FEE(S)

Non-English Specification, \$130 fee (no small entity discount)

Other (e.g., late filing surcharge): 1402 Filing a brief in support of an appeal 500.00

SUBMITTED BY			
Signature		Registration No. (Attorney/Agent)	46,746
Name (Print/Type)	Joseph T. Grunkemeyer	Telephone	(202) 404-1556
		Date	January 9, 2006

TRANSMITTAL OF APPEAL BRIEF			Docket No. 96202US1
In re Application of: Teddy M Keller et al.			
Application No. 10/808266-Conf. #4785	Filing Date March 17, 2004	Examiner D. Truong	Group Art Unit 1711
Invention: SYNTHESIS OF NOVEL OLIGOMERIC HYDROXY ARYLEETHERS, CONVERSION TO OLIGOMERIC ARYETHER CONTAINING PHTHALONITRILES AND POLYMERIZATION THEREOF			
<u>TO THE COMMISSIONER OF PATENTS:</u>			
Transmitted herewith is the Appeal Brief in this application, with respect to the Notice of Appeal filed: <u>October 14, 2005</u> .			
The fee for filing this Appeal Brief is <u>\$ 500.00</u> .			
<input checked="" type="checkbox"/> Large Entity <input type="checkbox"/> Small Entity			
<input type="checkbox"/> A petition for extension of time is also enclosed.			
The fee for the extension of time is _____ .			
<input type="checkbox"/> A check in the amount of _____ is enclosed.			
<input checked="" type="checkbox"/> Charge the amount of the fee to Deposit Account No. <u>50-0281</u> . This sheet is submitted in duplicate.			
<input type="checkbox"/> Payment by credit card. Form PTO-2038 is attached.			
<input checked="" type="checkbox"/> The Director is hereby authorized to charge any additional fees that may be required or credit any overpayment to Deposit Account No. <u>50-0281</u> . This sheet is submitted in duplicate.			
 _____ Joseph T. Grunkemeyer Attorney Reg. No. : 46,746 US NAVAL RESEARCH LABORATORY 4555 Overlook Ave, SW Washington, DC 20375 (202) 404-1556		Dated: <u>January 9, 2006</u>	

PATENT APPLICATION
Docket No.: NC 96,202IN THE UNITED STATES PATENT AND TRADEMARK OFFICE
BEFORE THE BOARD OF PATENT APPEALS AND INTERFERENCES

In the In the application of: Keller et al.

Serial No.: 10/808,266

Filed: 03/17/2004

For: OLIGOMERIC HYDROXY ARYLETHER PHTHALONITILES AND SYNTHESIS
THEREOF

Examiner: Truong, Duc

Art Group Unit: 1711

January 9, 2006

APPEAL BRIEF

The present appeal is taken from the final rejection of claims 14-21 and 38-56. The final rejection was mailed on 05/13/2005. A Notice of Appeal was filed on 10/14/2005. A copy of the claims on appeal, as amended in the 03/17/2004 Preliminary Amendment, is attached in the Appendix.

REAL PARTY IN INTEREST

The real party in interest is the United States Government, as represented by the Secretary of the Navy.

RELATED APPEALS AND INTERFERENCES

The present application and US Patent Application No. 10/808,264 are both divisional applications of the same parent application, US Patent 6,756,470. Both applications are under appeal.

STATUS OF CLAIMS

Claims 14-21 and 38-56 (all pending claims) are rejected.

STATUS OF AMENDMENTS

No amendments were filed after the final rejection.

01/10/2006 SSITHIB1 00000054 500281 10808266
01 FC:1402 500.00 DA

Serial No.: 10/808,266

PATENT APPLICATION
Docket No.: NC 96,202

SUMMARY OF CLAIMED SUBJECT MATTER

Independent claim 14 recites a thermoset formed by curing a mixture comprising a phthalonitrile monomer comprising the formula: $C_6(CN)_2H_3-O-Ar-(O-Ar)_n-C_6(CN)_2H_3$ (0017; 0016, line 3). Ar is an independently selected divalent aromatic radical (0013, line 4) with or without substituents containing one or more fused aromatic rings, one or more non-fused aromatic rings without intervening functional groups, or combinations thereof wherein the radical sites are on the same or different aromatic rings (0021, lines 2-5). The value n is an even integer greater than or equal to 2 (0016, lines 4-5).

Independent claim 38 recites a process of preparing a thermoset comprising the step of curing a mixture comprising the above phthalonitrile monomer (0017).

Independent claim 47 recites a process of preparing a thermoset comprising the steps of: reacting a dihydroxyaromatic with a dihaloaromatic (0015, line 7); reacting a 3- or 4-nitrophthalonitrile with the product of the previous step (0016, line 5-6); and curing a mixture comprising the product of the previous step (0017). The reaction is performed in the presence of a copper compound (0013, lines 6-7) and a base (0036, lines 5-6: Any base may be used in a subsequent step; 0058: The same base is used in both steps). The dihydroxyaromatic is present in an excess amount (0026, line 4).

There are no means plus function or step plus function limitations in any appealed claim.

GROUNDS OF REJECTION TO BE REVIEWED ON APPEAL

- A. Claims 14-21 and 38-46 stand rejected under 35 U.S.C § 103(a) as allegedly unpatentable over Keller et al. (US 4,259,471).
- B. Claims 47-56 stand rejected under 35 U.S.C § 103(a) as allegedly unpatentable over Keller (US 5,352,760 or US 5,464,926).

ARGUMENT

- A. Claims 14-21 and 38-46 recite subject matter that is not unpatentable under 35 U.S.C. § 103(a) over Keller ('471) as the reference is not enabling

Claims 14 (15-21 dependent thereon) and 38 (39-46 dependent thereon)

Serial No.: 10/808,266

PATENT APPLICATION
Docket No.: NC 96,202

Claim 14 is to a thermoset formed by curing a mixture comprising a phthalonitrile monomer $C_6(CN)_2H_3-O-Ar-(O-Ar)_n-C_6(CN)_2H_3$. Claim 38 is to the same method of making the thermoset. Keller discloses the structure $C_6(CN)_2H_3-(O-\phi)_x-O-C_6(CN)_2H_3$, where x is from 1 to 10. Note that when n is 2 in the present claims, x is 3 in Keller. When x is 3, 5, 7, or 9, the disclosed structure is within the scope of the presently claimed structure.

The reference is not enabling for all disclosed values of x, including 3, 5, 7, or 9. "Where a process for making the compound is not developed until after the date of invention, the mere naming of a compound in a reference, without more, cannot constitute a description of the compound." MPEP 2121.02, citing *In re Hoeksema*, 158 U.S.P.Q 596, 399 F.2d 269 (C.C.P.A. 1968). The reference merely states that the aromatic diols are easily made by an Ullman ether synthesis, and cites to Williams, et al. and Hammann et al. (both attached) for further information (col. 3, line 68-col. 4, line 8). The examples in Keller only disclose the use of compounds having x = 1 and 2 (n = 0 and 1), and no syntheses of aromatic diols needed for making the phthalonitrile are disclosed. Williams and Hammann do not disclose any aromatic diols at all, only short chains of aryl groups without the hydroxide groups needed to form the phthalonitrile. Since the instant claim requires that n be at least 2, none of the claimed compounds are enabled by Keller.

As an alternative basis for showing nonenablement of the reference, attached is the declaration of Teddy M. Keller stating his expert opinion that the Ullmann ether synthesis cannot be used to make oligomeric or polymeric aryl ethers in high yield and high molecular weight.

The Examiner stated that the declaration is not commensurate with the scope of the claims (Office Action of 05/16/2005, page 2, lines 18-19). It was not stated what part of the claim was not covered by the declaration. (In the interview of 12/15/2005 for related case 10/808,264, the Examiner stated that the same declaration was not persuasive because it is based on process steps, whereas claims 1 and 2 of 10/808,264 are product claims. The Examiner has not had the opportunity to comment on whether this position also applies to the present case.)

The relevant inquiry is not whether the statements of the declaration are commensurate with the scope of the claims, but it is whether the subject matter shown to be nonenabled is commensurate with the scope of the claims. The declaration states that "the Ullmann ether synthesis referred to in the Keller reference (US Patent No. 4,259,471) cannot be used to make oligomeric or polymeric aryl ethers in high yield and high molecular weight." (Paragraph 3.)

Serial No.: 10/808,266

PATENT APPLICATION
Docket No.: NC 96,202

Thus, the scope of the nonenabled subject matter covers all polymeric aryl ethers, which is another term for polyaromatic ethers. Claim 14 recites phthalonitriles made from polyaromatic ethers. The nonenabled subject matter is commensurate with the scope of the claims.

Claims 16

Claim 16 recites that n is 2, 4, 6, or 8. These specific values of n are not disclosed in Keller.

Claims 20, 21, 40, and 41

These claims recite that the polymerization mixture further comprises other phthalonitriles. Keller does not disclose copolymerizing the disclosed phthalonitrile with other phthalonitriles.

B. Claims 47-56 recite subject matter that is not unpatentable under 35 U.S.C. § 103(a) over Keller ('760 or '926)

Claim 47 (48-56 dependent thereon)

Keller discloses reacting a dihydroxyaromatic with a dihaloaromatic in the presence of a copper compound and a base, reacting a 3- or 4-nitrophthalonitrile with the product of the previous step, and curing a mixture comprising the product of the previous step.

In order to make a *prima facie* case of obviousness, each claim limitation must be disclosed in the references. None of the references discloses the limitation in claim 47 that the first step is performed in the presence of a copper compound. The Examiner cited to col. 6, line 48 of '760 as disclosing the copper compound. However, this copper compound is a curing agent in the final step of converting the phthalonitrile to a thermoset (col. 6, lines 34-36). The copper is not present when reacting the dihydroxyaromatic with a dihaloaromatic. The significance of the copper in the present invention is that it allows for the reaction without an activating group in the reactants. In Keller, the dihaloaromatic contains an R group that is an electron-withdrawing group ('760, col. 2, lines 19-48). The reaction disclosed in Keller would not occur without the electron-withdrawing group. As all the claim limitations of claim 47 are not disclosed in the references, a *prima facie* case of obviousness has not been made.

Serial No.: 10/808,266

PATENT APPLICATION
Docket No.: NC 96,202

The Examiner admitted that the references do not disclose a copper compound in the first step (final rejection, p.3, lines 8-9). However, the Examiner stated that this is "not found persuasive as since they all form the same products." (Advisory action, item 11.) The Examiner is inappropriately citing to a product in the reference as disclosing a process step in the present claims.

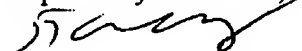
The Examiner also stated that "Applicant's arguments are also based on the reactants in that the references disclose a dihaloaromatic group containing an R group that is an electron-withdrawing group. This is incorrect in stating that (see non-final office action)." (Advisory action, item 11.) Nowhere else in the record is the presence of the electron-withdrawing group disputed by the Examiner. This argument does not restrict the claim to particular reactants, but only explains that the copper compound allows for a greater range of reactants. Applicants' primary argument regarding the lack of a *prima facie* case remains that the process step of using copper is not disclosed in the references.

CONCLUSION

For the reasons stated above, reversal of the rejections under 35 U.S.C. § 103 is earnestly solicited.

In the event that a fee is required, please charge the fee to Deposit Account No. 50-0281, and in the event that there is a credit due, please credit Deposit Account No. 50-0281.

Respectfully submitted,



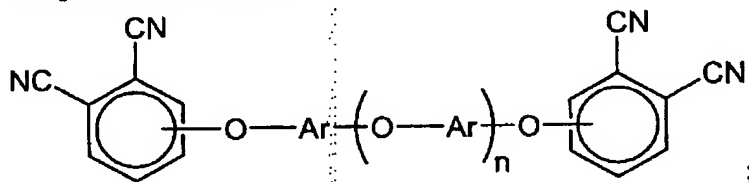
Joseph T. Grunkemeyer
Reg. No. 46,746
Phone No. 202-404-1556
Office of the Associate Counsel
(Patents), Code 1008.2
Naval Research Laboratory
4555 Overlook Ave, SW
Washington, DC 20375-5325

Serial No.: 10/808,266

PATENT APPLICATION
Docket No.: NC 96,202

APPENDIX-THE CLAIMS ON APPEAL

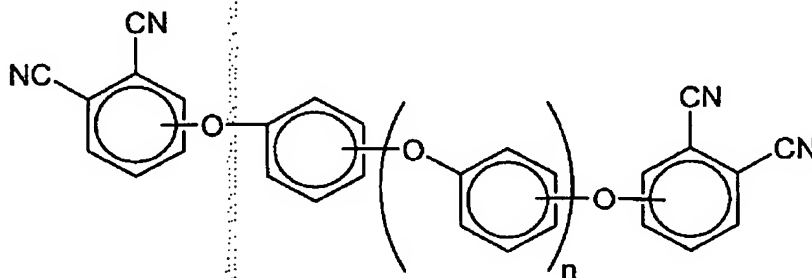
14. A thermoset formed by curing a mixture comprising a phthalonitrile monomer comprising the formula:



wherein Ar is an independently selected divalent aromatic radical with or without substituents containing one or more fused aromatic rings, one or more non-fused aromatic rings without intervening functional groups, or combinations thereof wherein the radical sites are on the same or different aromatic rings; and

wherein n is an even integer greater than or equal to 2.

15. The thermoset of claim 14, wherein n is less than or equal to about 100.
16. The thermoset of claim 14, wherein n is selected from the group consisting of 2, 4, 6, and 8.
17. The thermoset of claim 14, wherein the phthalonitrile monomer comprises the formula:

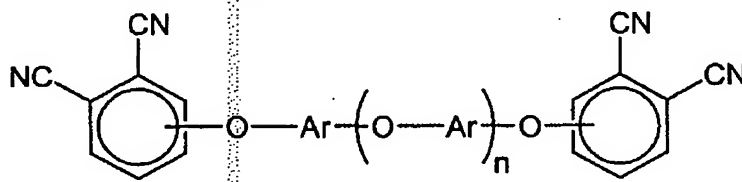


18. The thermoset of claim 14, wherein the mixture comprises more than one phthalonitrile monomer.

Serial No.: 10/808,266

PATENT APPLICATION
Docket No.: NC 96,202

19. The thermoset of claim 18, wherein the more than one phthalonitrile monomers comprise more than one value for n.
20. The thermoset of claim 14, wherein the mixture further comprises a compound selected from the group consisting of 4,4'-bis(3,4-dicyanophenoxy)biphenyl, bis[4-(3,4-dicyanophenoxy)phenyl]dimethylmethane, bis[4-(2,3-dicyanophenoxy)phenyl]dimethylmethane, bis[4-(3,4-dicyanophenoxy)phenyl]-bis(trifluoromethyl)methane, bis[4-(2,3-dicyanophenoxy)phenyl]-bis(trifluoromethyl)methane, 1,3-bis(3,4-dicyanophenoxy)benzene, and 1,4-bis(3,4-dicyanophenoxy)benzene.
21. The thermoset of claim 14, wherein the mixture further comprises a compound with one or more phthalonitrile groups.
38. A process of preparing a thermoset comprising the step of curing a mixture comprising a phthalonitrile monomer comprising the formula,



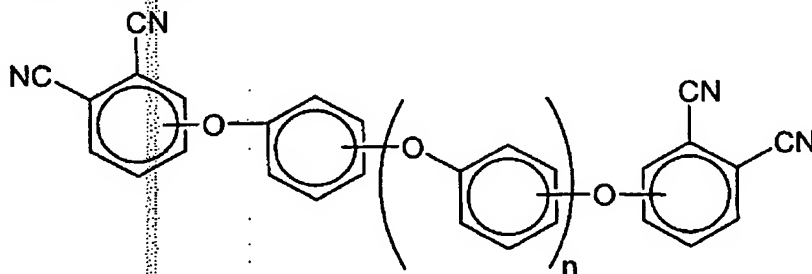
wherein Ar is an independently selected divalent aromatic radical with or without substituents containing one or more fused aromatic rings, one or more non-fused aromatic rings without intervening functional groups, or combinations thereof wherein the radical sites are on the same or different aromatic rings; and

wherein n is an even integer greater than or equal to 2.

Serial No.: 10/808,266

PATENT APPLICATION
Docket No.: NC 96,202

39. The process of claim 38, wherein the phthalonitrile monomer comprises the formula:



40. The process of claim 38, wherein the mixture comprises more than one phthalonitrile monomer.
41. The process of claim 39, wherein the more than one phthalonitrile monomers comprise more than one value for n.
42. The process of claim 38, wherein the mixture further comprises a compound selected from the group consisting of 4,4'-bis(3,4-dicyanophenoxy)biphenyl, bis[4-(3,4-dicyanophenoxy)phenyl]dimethylmethane, bis[4-(2,3-dicyanophenoxy)phenyl]dimethylmethane, bis[4-(3,4-dicyanophenoxy)phenyl]-bis(trifluoromethyl)methane, bis[4-(2,3-dicyanophenoxy)phenyl]-bis(trifluoromethyl)methane, 1,3-bis(3,4-dicyanophenoxy)benzene, and 1,4-bis(3,4-dicyanophenoxy)benzene.
43. The process of claim 38, wherein the mixture further comprises a compound with one or more phthalonitrile groups.
44. The process of claim 38, wherein the mixture further comprises a curing agent.

Serial No.: 10/808,266

PATENT APPLICATION
Docket No.: NC 96,202

45. The process of claim 44, wherein the curing agent comprises a composition selected from the group consisting of aromatic amines, primary amines, secondary amines, diamines, polyamines, amine-substituted phosphazenes, phenols, strong acids, organic acids, strong organic acids, inorganic acids, metals, metallic salts, metallic salt hydrates, metallic compounds, halogen-containing aromatic amines, clays, and chemically modified clays.
46. The process of claim 44, wherein the curing agent is selected from the group consisting of bis[4-(4-aminophenoxy)phenyl]sulfone, 1,4-bis(3-aminophenoxy)benzene, 1,12-diaminododecanediphenylamine, epoxy amine hardener, 1,6-hexanediamine, 1,3-phenylenediamine, p-toluenesulfonic acid, cuprous iodide, cuprous bromide, stannous chloride, stannous chloride hydrates, stannous chloride dihydrate, aluminum nitrate hydrates, aluminum nitrate nonahydrate, montmorillonite, and chemically modified montmorillonite.
47. A process of preparing a thermoset comprising the steps of:
reacting a dihydroxyaromatic with a dihaloaromatic;
wherein the reaction is performed in the presence of a copper compound and a base; and
wherein the dihydroxyaromatic is present in an excess amount;
reacting a 3- or 4-nitrophthalonitrile with the product of the previous step; and
curing a mixture comprising the product of the previous step.
48. The process of claim 47:
wherein the dihydroxyaromatic is selected from the group consisting of resorcinol, hydroquinone, and combinations thereof; and
wherein the dihaloaromatic is selected from the group consisting of m-dibromobenzene, p-dibromobenzene, m-diiodobenzene, p-diiodobenzene, m-bromiodobenzene, p-bromiodobenzene, and combinations thereof.

Serial No.: 10/808,266

PATENT APPLICATION
Docket No.: NC 96,202

49. The process of claim 47, wherein the copper compound is selected from the group consisting of CuI and CuBr.
50. The process of claim 47, wherein the mixture comprises more than one phthalonitrile monomer.
51. The process of claim 47, wherein the mixture further comprises a compound selected from the group consisting of 4,4'-bis(3,4-dicyanophenoxy)biphenyl, bis[4-(3,4-dicyanophenoxy)phenyl]dimethylmethane, bis[4-(2,3-dicyanophenoxy)phenyl]dimethylmethane, bis[4-(3,4-dicyanophenoxy)phenyl]-bis(trifluoromethyl)methane, bis[4-(2,3-dicyanophenoxy)phenyl]-bis(trifluoromethyl)methane, 1,3-bis(3,4-dicyanophenoxy)benzene, and 1,4-bis(3,4-dicyanophenoxy)benzene.
52. The process of claim 47, wherein the mixture further comprises a compound with one or more phthalonitrile groups.
53. The process of claim 47, wherein the mixture further comprises a curing agent.
54. The process of claim 53, wherein the curing agent is selected from the group consisting of aromatic amines, primary amines, secondary amines, diamines, polyamines, amine-substituted phosphazenes, phenols, strong acids, organic acids, strong organic acids, inorganic acids, metals, metallic salts, metallic salt hydrates, metallic compounds, halogen-containing aromatic amines, clays, and chemically modified clays.

Serial No.: 10/808,266

PATENT APPLICATION
Docket No.: NC 96,202

55. The process of claim 53, wherein the curing agent is selected from the group consisting of bis[4-(4-aminophenoxy)phenyl]sulfone, 1,4-bis(3-aminophenoxy)benzene, 1,12-diaminododecanediphenylamine, epoxy amine hardener, 1,6-hexanediamine, 1,3-phenylenediamine, p-toluenesulfonic acid, cuprous iodide, cuprous bromide, stannous chloride, stannous chloride hydrates, stannous chloride dihydrate, aluminum nitrate hydrates, aluminum nitrate nonahydrate, montmorillonite, and chemically modified montmorillonite.
56. The process of claim 47, wherein the base is selected from the group consisting of cesium carbonate and potassium carbonate.

Serial No.: 10/808,266

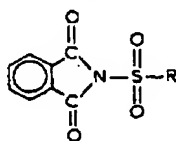
PATENT APPLICATION
Docket No.: NC 96,202

APPENDIX-EVIDENCE

Hammann et al., "Synthesis of Seven New Polyphenyl Ethers" *J. Chem. and Eng. Data*, 15(2), 352 (1970), cited in Keller reference.

Williams et al., (Solvent-Assisted Ullmann Ether Synthesis. Reaction of Dihydric Phenols" *J. Org. Chem.*, 32, 2501 (1967), cited in Keller reference.

Declaration under 37 C.F.R. § 1.132 of Teddy M. Keller

Table I. *N*-Alkyl- and *N*-Arylsulfonylphthalimides

R	Recryst. Solvent ^a	Yield, % ^b	M.P., °C.	Analysis, %			
				N		S	
				Calcd.	Found	Calcd.	Found
Methyl	A	62	228.5-30	6.22	6.28	14.24	14.27
Ethyl	B	65	181.5-82	5.85	5.86	13.40	13.55
<i>n</i> -Propyl	C	62	139-39.5	5.53	5.51	12.66	12.69
<i>n</i> -Butyl	C	60	114.5-15	5.24	5.27	12.00	11.92
Phenyl	D	74	202.5-03.5 ^c				
<i>p</i> -Tolyl	E	75	238-40 ^d				
<i>p</i> -Bromophenyl	E	70	247-48 ^e				
β -Naphthyl	E	73	218-19 ^f				

^a A, acetonitrile; B, acetonitrile-benzene; C, benzene; D, toluene; E, xylenes (b.p. 135-40° C.). ^b Yields are for purified products. ^c Lit. (2) m.p. 206° C. ^d Lit. (2) m.p. 237° C. ^e Lit. (2) m.p. 246° C. ^f Lit. (2) m.p. 218° C.

Reaction of Potassium Phthalimide with Sulfonyl Chlorides. All of the compounds listed in Table I were prepared in the same manner. A stirred mixture of 0.0050 mole of potassium phthalimide and 0.0050 mole of the appropriate sulfonyl chloride in 20 ml. of acetonitrile was heated under reflux for 1 hour. After cooling to ambient temperature, the mixture was poured into 100 ml. of cold water. The white solid, which separated immediately, was removed by filtration, washed with water, and dried. The crude products were purified by one or two recrystallizations from the solvents indicated in Table I.

Each *N*-substituted phthalimide was found to be identical with an authentic sample, which was prepared by the reaction of the appropriate sulfonamide with phthaloyl chloride according to the method of Evans and Dehn (1), by mixture melting point determination and infrared spectra comparison.

In experiments that involved methane- and butane-1-sulfonyl chlorides, small amounts of a solid—32 and 20 mg., respectively—precipitated from the aqueous filtrates on standing overnight. This solid was identified by mixture

melting point determination and infrared spectra comparison as phthalimide.

ACKNOWLEDGMENT

The author is indebted to Alan R. Oyler for technical assistance.

LITERATURE CITED

- (1) Evans, T.W., Dehn, W.M., *J. Am. Chem. Soc.* 51, 3651 (1929).
- (2) Evans, T.W., Dehn, W.M., *Ibid.*, 52, 2531 (1930).
- (3) Köhle, E., Wegler, R., *Ann.* 616, 183 (1958).
- (4) Nefkens, G.H.L., Tesser, G.I., Nivard, R.J.F., *Rec. Trav. Chim.* 79, 688 (1960).
- (5) Optiz, G., *Angew. Chem. Intern. Ed. Engl.* 6, 107 (1967).
- (6) Salzberg, P.L., Supniewski, J.V., "Organic Syntheses," Coll. Vol. I, p. 119, Wiley, New York, 1941.
- (7) Scott, R.B., Jr., Lutz, R.E., *J. Org. Chem.* 19, 830 (1954).

RECEIVED for review August 4, 1969. Accepted November 29, 1969.

Synthesis of Seven New Polyphenyl Ethers

WILLIAM C. HAMMANN and ROBERT M. SCHISLA
Monsanto Co., St. Louis, Mo. 63166

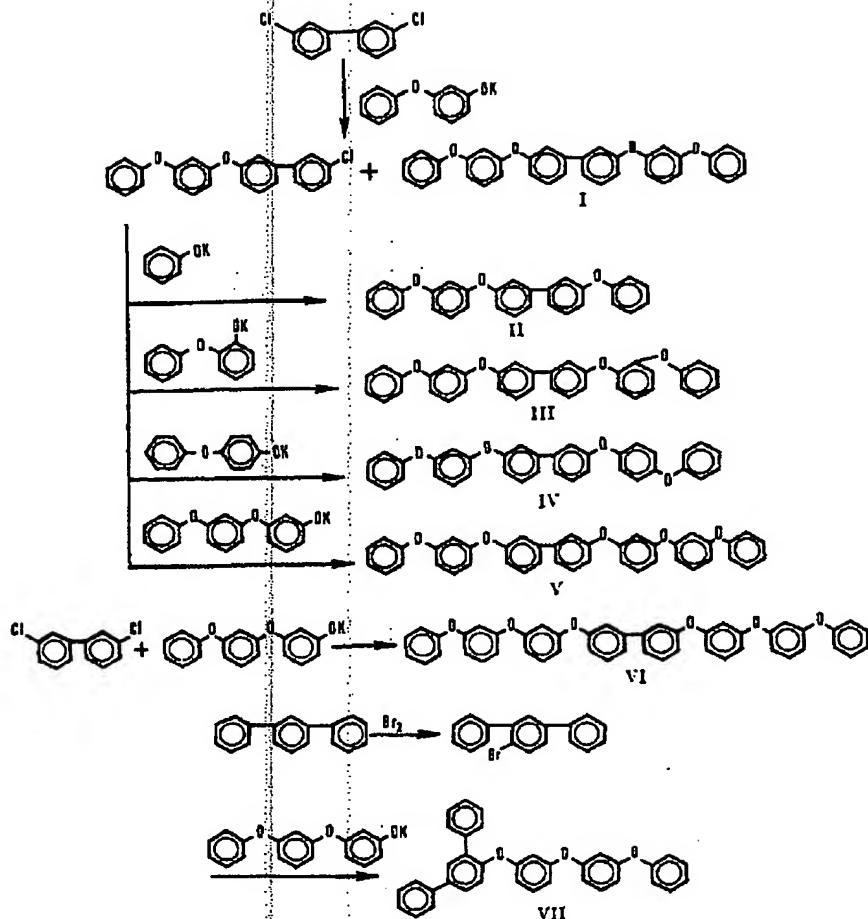
JOHN S. ADAMS, JR.,¹ and STANLEY D. KOCH¹
Monsanto Research Corp., Dayton Laboratory, Dayton, Ohio 45407

Seven new polyphenyl ethers were synthesized, using a modified Ullmann reaction. Per cent yields, physical properties, and elemental analyses are given.

POLYPHENYL ethers show excellent thermal stability and are used as high-temperature functional fluids, finding application as heat transfer agents. In addition, they have proved useful as the liquid phase in high-temperature chro-

matographic work (3-5, 7). Seven new polyphenyl ethers containing a biphenyl central core were synthesized in these laboratories. The synthetic routes used were similar in each case and involved a modified Ullmann reaction. The mechanism and parameters of this reaction have been studied in detail by a number of workers (1, 2, 8, 9). The reaction schemes leading to each compound are depicted below:

¹Present address, Horizons Research, Inc., Cleveland, Ohio 44104



EXPERIMENTAL

The phenols used in the syntheses were obtained from Monsanto Co.'s Central Research Department, and were used without further purification. Santowax-M, also obtained from Monsanto Co., was used as received in the preparation of 4'-bromo-*m*-terphenyl, intermediate for VII, 4'-[*m*-(*m*-phenoxyphenoxy)phenoxy]-*m*-terphenyl. Monsanto Co. also supplied the key intermediate 3,3'-dichlorobiphenyl used in six of the seven syntheses. As received, it was 87% pure, and was further purified by careful fractionation through a 90-cm Vigreux column, followed by topping this distillate, to give 200 grams of 98.7% pure material, considered suitable for synthetic use. The major impurity was 3-chlorobiphenyl.

3,3'-Bis(*m*-phenoxyphenoxy)biphenyl (I) and Key Intermediate, 3-Chloro-3'-(*m*-phenoxyphenoxy)biphenyl. A 500-ml four-necked flask equipped with stirrer, thermometer, and Dean-Stark trap surmounted by a Friedrichs condenser was charged with 93.5 grams (0.505 mole) of *m*-phenoxyphenol, and 30.8 grams (0.50 mole) of potassium hydroxide (assumed in all reactions to be 81% pure) was added in increments with stirring at 100°C. After the initial exothermic reaction had subsided, 80 ml of toluene was added, and water was azeotroped from the reaction mixture until the theoretical amount had been collected, including that from the potassium hydroxide.

The toluene was distilled from the reaction mixture until the pot temperature reached 230°C. After cooling to 150°C., 100 ml of diglyme was added, together with 7 grams of

cuprous chloride and 2 grams of copper powder. The reaction mixture was then heated with stirring to 170°C., and 129.3 grams (0.57 mole) of 3,3'-dichlorobiphenyl was added over a 1-hour period. Diglyme was distilled from the reaction mixture until the pot temperature reached 235°C., when reaction was continued for 18 hours. On cooling, the reaction mixture was diluted with an equal volume of ether, and filtered to remove copper and potassium salts. The ethereal solution was washed three times with 150-ml portions of 20% potassium hydroxide, followed by water washing until neutral. The water and potassium hydroxide layers were extracted with additional ether. The ether solutions were combined and dried over anhydrous magnesium sulfate. After filtration and removal of ether on the rotary evaporator, the dark red-brown oil was distilled to yield 47.2 grams of starting 3,3'-dichlorobiphenyl, bp 112-14°C./0.05 mm; 6.2 grams of intermediate fractions, bp 127-202°C./0.03 mm; 71.4 grams (38%) of 3-chloro-3'-(*m*-phenoxyphenoxy)biphenyl, bp 220-2°C./0.04 mm; 20.4 grams of intermediate cuts, bp 223-302°C./0.06 mm; and 17.2 grams of 3,3'-bis(*m*-phenoxyphenoxy)biphenyl (I), bp 312°C./0.05 mm. A pot residue of 8.9 grams remained. Final purification of I was effected by dissolving it in ethyl ether and treating it with 1.0 gram of activated charcoal, followed by filtration through filter aid, removal of ethyl ether on the rotary evaporator, and prolonged treatment in a vacuum oven at 100-10°C./0.1 mm.

3-(*m*-Phenoxyphenoxy)-3'-(*p*-phenoxyphenoxy)biphenyl (IV). This preparation is typical of the syntheses leading to the other three polyphenyl ethers using the same key chloro-

Table I. Yields, Physical Properties, and Elemental Analyses of Polyphenyl Ethers

Compound	% Yield	BP, °C./Mm.	MP, °C.	n_D^{25}	d_4^{25}	Analysis {	
						Calcd.	Found
						C	H
I	13 ^a	312/0.05	85-88	1.6520	...	82.7	5.0
						82.4	5.2
II	56 ^a	248-53/0.06	...	1.6474	1.184	83.7	5.2
						83.2	5.2
III	61 ^a	255-60/0.02	...	1.6480	1.197	82.7	5.0
						83.0	5.3
IV	62 ^a	302-07/0.05	...	1.6500	1.201	82.7	5.0
						82.5	5.1
V	76 ^a	340/0.05	...	1.6510	1.219	82.0	4.9
						81.8	5.0
VI	25 ^b ; 15 ^c	1.658(9)	1.231	81.5	4.9
						81.6	5.0
VII	69 ^a	337/0.07	...		1.185	83.2	5.2
						85.4	5.2

^a Calculated from weight of distilled material. ^b Based on total product recovered. ^c Based on purified product. ^d Could not be determined at 25° C.

phenoxybiphenyl, but varying the phenol. Work-up in every one of the four cases was virtually identical, the products differing only in boiling point and the other intrinsic physical properties given in Table I. Yields for the four compounds varied from 58-76%, also shown in Table I.

A 250-ml reaction flask equipped with stirrer, dropping funnel, thermometer, and Dean-Stark trap surmounted by a Friedrichs condenser was charged with 200 grams (1.07 mole) of *p*-phenoxyphenol, and 34.9 grams (0.567 mole) of potassium hydroxide was added in increments at 90° C. To the resulting melt was added 50 ml of toluene. The theoretical amount of water was azeotroped from the reaction mixture, followed by removal of toluene up to 230° C. On cooling to 150° C., the reaction mixture was diluted with 150 ml of diglyme, and 5.0 grams of cuprous chloride and 1.0 gram of copper powder were added. Over a 45-minute period, 20 grams (0.054 mole) of 3-chloro-3'-(*m*-phenoxyphenoxy)biphenyl in diglyme was added, and the diglyme was removed by distillation. The stirred reaction mixture was heated at 235° C. for 19 hours. On cooling, an equal volume of ether was added and this mixture was centrifuged to remove salts. The ethereal solution was washed with 25% potassium hydroxide solution to remove excess phenol, and with water until neutral. It was then dried over anhydrous magnesium sulfate.

After filtration and concentration to remove ether, the oil obtained was distilled. One unweighted cut, bp 110-297° C./0.05 mm, was taken, followed by 17.5 grams of product, bp 297-302° C./0.05 mm. Final purification of this material was the same as that described above for I.

3,3'-Bis[*m*-(*m*-phenoxyphenoxy)phenoxy]biphenyl (VI). A 250-ml four-necked flask, equipped with stirrer, dropping funnel, thermometer, and Dean-Stark trap surmounted by a Friedrichs condenser, was charged with 69.8 grams (0.215 mole) of *m*-(*m*-phenoxyphenoxy)phenol, to which 13.0 grams (0.208 mole) of potassium hydroxide was added at 90° C., followed by addition of 50 ml of toluene. The stirred reaction mixture was heated to azeotrope water, followed by distillation of toluene until the temperature of the reaction mixture reached 230° C. After cooling, 50 ml of diglyme, 2.5 grams of cuprous chloride, 0.5 gram of copper powder, and 20 grams (0.09 mole) of 3,3'-dichlorobiphenyl were added to this mixture over a 30-minute period at 175° C. Diglyme was distilled from the reaction mixture, which was then heated at 230-60° C. for 18 hours. The cooled, very thick, semisolid mass resulting was dissolved in 500 ml of ethyl ether, and the suspended salts were removed by centrifugation. The resulting ethereal solution was washed thoroughly with 10% potassium hydroxide solution and with water

until neutral, and was finally dried over anhydrous magnesium sulfate. After concentrating this solution, it was distilled using a 100-ml distilling flask connected to a 25-cm heated Vigreux column with direct take-off head attached to a fraction cutter. A fraction amounting to 7.0 grams, bp 136-293° C./0.06 mm, was obtained initially. The distillate, after cooling, was transferred to a 25-ml "mini-ware" still pot attached to a Claisen head and "mini-ware" fraction cutter. Distillation using a Wood's metal bath on the still pot gave 10 grams of viscous red-orange liquid, bp 348-52° C./0.09 mm, at a pot temperature of 428° C. Elemental analysis showed this cut to be about 80% desired product and 20% of presumably 3-chloro-3'-(*m*-(*m*-phenoxyphenoxy)phenoxy)biphenyl. Since 450° C. would be an upper limit for many of the ethers with regard to accelerated thermal decomposition, it was decided not to attempt to distill the remainder of the pot residue, amounting to 11 grams. Instead, this black glass (at room temperature) was dissolved in 300 ml of ethyl ether, treated with 1 gram of activated charcoal, and filtered through filter aid to give an orange fluorescent solution which, on concentration, gave a dark red-orange viscous liquid. The treatment was repeated, using 125 ml of ethyl ether and 0.5 gram of charcoal. After the ether was removed on the rotary evaporator, the orange liquid was placed in a vacuum oven for 16 hours at 110° C./0.1 mm and finally 1 hour at 125° C./0.1 mm to give 9.8 grams of light orange product. Although not determined, we estimate by extrapolation from the boiling points of the closely related five-, six-, and seven-ring ethers prepared that this eight-ring ether would have bp ~380-90° C./0.05 mm.

4'-(*m*-(*m*-Phenoxyphenoxy)phenoxy)-*m*-terphenyl (VII). Synthesis of 4'-bromo-*m*-terphenyl was carried out by the procedure of Schmidt *et al.* (6). Product was purified by preparative vapor phase chromatography, using an F&M Model 775 chromatographic unit, incorporating a 6.5-ft x 4-inch column packed with 20% UCW98 on Chromosorb W. Injection port and detector temperatures were 340° C., with column temperature at 240° C. The resulting product was calculated to be 99+% pure by vpc.

A 500-ml flask equipped with dropping funnel, stirrer, thermometer, and a Dean-Stark trap surmounted by a Friedrichs condenser was charged with 100 grams (0.36 mole) of *m*-(*m*-phenoxyphenoxy)phenol and 9.5 grams of potassium hydroxide. The reaction mixture was heated with stirring until the potassium hydroxide had completely dissolved. Then 250 ml of toluene was added to azeotrope the theoretical amount of water. Toluene was distilled from the system until the temperature reached 200° C. After

the temperature of the reaction mixture had returned to 150°C, 100 ml of diglyme was added, together with 2.5 grams of cuprous chloride and 0.5 gram of copper powder.

The temperature was gradually increased to 160°C. and 20.6 grams (0.087 mole) of 4'-bromo-*m*-terphenyl, dissolved in 40 ml of diglyme, was added dropwise. The reaction was allowed to continue for 10 hours at 185°C. It was then diluted with ethyl ether and filtered. The ether layer was washed with 2 × 100 ml of 25% aqueous potassium hydroxide, followed by water washing until neutral. The aqueous washes were extracted with 2 × 100 ml of ethyl ether. The ether layers were combined, washed with distilled water until neutral, dried over magnesium sulfate, and filtered. A brown viscous liquid was obtained upon removal of the ether. This material was distilled to obtain 10 grams of forecut, bp 80–837°C./0.07 mm, and 23.5 grams of 4'-[*m*-(*m*-phenoxyphenoxy)phenoxy]-*m*-terphenyl, bp 337°C./0.07 mm., as a yellow viscous liquid.

Final purification was effected as described above for the other ethers prepared.

ACKNOWLEDGMENT

Elemental analyses were performed by Galbraith Laboratories, Knoxville, Tenn. Technical assistance was expertly provided by Percival A. DeChamp.

LITERATURE CITED

- (1) Brown, G. F., Goldman, A., *Polymer Preprints* 4 (2), 39 (1963).
- (2) Brown, G. F., Goldman, A., *Ibid.*, 5 (1), 196 (1964).
- (3) Chang, T. C., Karr, C., *Anal. Chim. Acta* 26 (5), 410 (1962).
- (4) Henbest, H. B., Reid, J. A. W., Stirling, C. J. M., *J. Chem. Soc.* 1961, p. 5239.
- (5) Richardson, G. A., Blake, E. S., *Ind. Eng. Chem. Prod. Res. Develop.* 7, 22 (1968).
- (6) Schmidt, J. J. E., Krimmel, J. A., Farrell, Jr., T. J., *J. Org. Chem.* 25, 252 (1960).
- (7) von Rudloff, E., *Can. J. Chem.* 38, 631 (1960).
- (8) Weingarten, J., *J. Org. Chem.* 29, 3624 (1964).
- (9) Williams, A. L., Kinney, R. E., Bridger, R. F., *Ibid.*, 32, 2501 (1967).

RECEIVED for review August 21, 1969. ACCEPTED December 15, 1969.

3,3'-Biscoumarins

LOYD L. WOODS and SAMIR M. SHAMMA
Texas Southern University, Houston, Tex. 77004

Five 3,3'-biscoumarins, none of which have been reported previously, were synthesized by a modification of the Perkin reaction.

A MIXTURE consisting of 0.1 mole of anhydrous powdered potassium succinate and 0.2 mole of the aldehyde was thoroughly mixed with 40 ml. of acetic anhydride in a flask and then heated in a Hi-Temp oil bath, already at equilibrium between 155° and 160°C. for 80 to 45 minutes. The mixtures were diluted with 300 ml. of water, cooled, and filtered and the precipitates dried in air. The compounds

were powdered and dried 3 days in a vacuum desiccator over Drierite.

A sample of each compound was purified by extraction with heptane, then ethyl acetate, and finally with boiling ethanol. The samples thus purified gave the analyses and infrared data shown in Table I.

One gram of compound 1 after having been treated as

Table I. Biscoumarins

Aldehyde Used	M.P., °C.	Yield, %	Formula	Calculated			Found		
				C	H	Other	C	H	Other
1. Salicylaldehyde	328	97	C ₁₂ H ₈ O ₄	74.47	3.47		74.66	3.69	
2. 5-Chloro-salicylaldehyde	>360	98	C ₁₁ H ₅ ClO ₄	60.19	2.24	19.74(Cl)	59.89	2.36	19.75(Cl)
3. 3-Methoxy salicylaldehyde	346–348	99	C ₁₀ H ₁₀ O ₄	68.56	4.02		68.36	4.06	
4. 2-Hydroxy-1-naphthaldehyde	>360	97	C ₁₆ H ₁₀ O ₄	79.99	3.61		80.28	3.82	
5. 5-Bromo-salicylaldehyde	>360	100	C ₁₁ H ₇ BrO ₄	48.25	1.79	35.66(Br)	48.53	2.01	35.77(Br)
1. 3,3'-Biscoumarin-1703*									
2. 6,6'-Dichloro-3,3'-biscoumarin-1707									
3. 8,8'-Dimethoxy-3,3'-biscoumarin-1707									
4. 2,2'-Bis(3H-naphtho[2,1-b]pyran-3,3'-dione-1710									
5. 6,6'-Dibromo-3,3'-biscoumarin-1716									

* Carbonyl absorption of infrared spectrum in cm.⁻¹ KBr pellet taken on Beckman IR-8.

AUGUST 1967

SOLVENT-ASSISTED ULLMANN ETHER SYNTHESIS

2501

(+)- α -phenylethylammonium O-benzyl-(*R*)-(-)-mandelate, 13136-59-9; O-benzyl-(*R*)-(-)-mandelamide, 13136-60-2.

Acknowledgment.—We are indebted to the National Institutes of Health (Grant No. GM-06232-06) for its generous support of a portion of this study.

Solvent-Assisted Ullmann Ether Synthesis. Reactions of Dihydric Phenols

A. L. WILLIAMS, R. E. KINNEY, AND R. F. BRIDGER

Mobil Oil Corporation, Central Research Division Laboratory, Princeton, New Jersey 08540

Received February 14, 1967

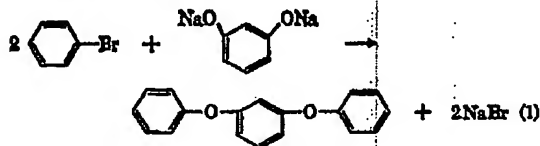
Certain organic solvents containing heteroatoms dissolve copper salts to form complexes which are catalytic in the Ullmann ether synthesis, thus allowing use of lower temperatures. When oxygen and water are excluded, salts of dihydric phenols can be allowed to react. By proper choice of solvent and conditions, the reaction can be directed toward polyphenyl ethers or phenolic ethers. Although resorcinol yields only tars under the usual melt conditions, the present system permits formation of *meta*-linked ethers in good yields. Rates of reaction of substituted bromobenzenes with disodium resorcinate in pyridine indicate nucleophilic attack by resorcinate dianion. Bromination of *m*-diphenoxybenzene under mild conditions led only to 2,4-diphenoxybromobenzene. This was condensed with various phenolic salts to synthesize a new class of nonlinear polyphenyl ethers

Although polyphenyl ethers are resistant to thermal, oxidative, and radiation damage,¹ their useful temperature range as fluids is restricted by the high melting points of the pure isomers. This problem is alleviated by employing mixtures of isomers, but liquid mixtures result only when a high proportion of the ether linkages are in the *meta* positions of the benzene rings.²

Low molecular weight polyphenyl ethers are usually prepared by the Ullmann ether synthesis.³ Copper metal is the preferred catalyst and the phenate melt is exposed to air to convert the copper to an active form. When *meta*-linked ethers are sought, the synthesis of *m*-diphenoxybenzene illustrates the main problems encountered. The first choice is whether the middle ring shall be derived from *m*-dibromobenzene or from resorcinol. Pure *m*-dibromobenzene is not readily available and attempts to employ resorcinol directly in the Ullmann ether synthesis have been reported to yield only tars.^{4,5} Failure to obtain polyphenyl ethers was ascribed to instability of the alkali metal salts of dihydric phenols at the temperature required for reaction.

Results and Discussion

With dry nitrogen to provide an inert atmosphere, cuprous chloride as catalyst, and pyridine as solvent, the disodium salt of resorcinol was converted to *m*-diphenoxybenzene in one step (eq 1). The yield of



recrystallized product was 70% (based on resorcinol). Details are given in experimental method A. The

product is accompanied by a small yield of *m*-phenoxyphenol, which is an intermediate, as the sodium salt. The formation of *m*-phenoxyphenol and its further conversion were observed by gas chromatography during the course of the reaction. Oxygen must be rigorously excluded as it causes formation of tars at the expense of product. Phenolic salts, free of water and alcohol, are conveniently prepared from sodium methoxide. This reactant was used as described in method A for the preparation of all disalts except for those few cases where another method is specifically mentioned. An excess of base completely inhibits the reaction by destroying the copper catalyst. Reactions were therefore carried out by using only 95% of the theoretical quantity of base to make the disalt.

Solvent-Catalyst Interactions.—Successful solvents for the ether condensation must not only dissolve the reactants, but bring the copper catalyst into solution as well. Various cupric salts (chloride, bromide, sulfate, acetylacetonate) were catalytic when dissolved in solvents which brought them into solution with the formation of coordination complexes (Table I). Copper

TABLE I
SOLVENTS IN THE PREPARATION OF *m*-DIPHENOXYBENZENE

Solvent for reaction at 125°	Yield from disodium resorcinate in 6 hr, %	
	<i>m</i> -Diphenoxy- benzene	<i>m</i> -Phenoxy- phenol
Pyridine (117°)	74	15
Pyridine + 2% water (112°)	4	23
2,4,6-Collidine	17	25
Pyridine <i>N</i> -oxide	18	40
Di- <i>n</i> -butylamine	32	19
1-Methyl-2-pyrrolidinone	11	46
Dimethylformamide	4	34
Hexamethylphosphoramide	5	47
Methyl sulfoxide	14	42
<i>n</i> -Propyl sulfone	42	33
Bis(2-methoxyethyl) ether	21	25

metal and cuprous oxide did not dissolve and did not promote the reaction. If copper acts as catalyst by forming a complex with the aryl bromide, it would appear that full coordination with solvent would be undesirable. Taking pyridine with cuprous chloride as

(1) C. L. Mahoney, E. R. Barnum, W. W. Karlin, K. J. Sax, and W. S. Saari, *J. Chem. Eng. Data*, **5**, 172 (1960).

(2) C. L. Mahoney and E. R. Barnum, "Synthetic Lubricants," R. C. Gunderson and A. W. Hart, Eds., Reinhold Publishing Corp., New York, N. Y., 1962, pp 402-460.

(3) P. Ullmann and P. Sponagel, *Ann.*, **480**, 83 (1906).

(4) K. J. Sax, W. S. Saari, C. L. Mahoney, and J. M. Gordon, *J. Org. Chem.*, **25**, 1590 (1960).

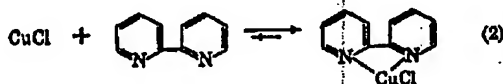
(5) G. P. Brown, S. A. Aftergut, and R. J. Blackington, *J. Chem. Eng. Data*, **6**, 125 (1961).

TABLE II
 p-SUBSTITUTED DIPHENOXYBENZENES FROM RESORCINOL

R group	Registry no.	Hr at 115°	Yield, %	Mp, °C	Carbon, %		Hydrogen, %	
					Calcd	Found	Calcd	Found
C ₆ H ₅ O	1638-12-6	8	68	84.7-85.1 ^a	80.69	80.50	4.97	5.06
CH ₃ O	13118-91-7	10	58	83.4-83.8	74.52	74.01	5.63	5.71
CH ₃ CO	13118-92-8	6	60	95.8-96.3	76.29	76.03	5.24	5.22
CH ₃	13131-51-6	10	61	c	82.73	82.41	6.25	6.23
Cl	13118-93-9	10	34	d	65.27	64.97	3.65	3.53
NO ₂	13118-94-0	5	63	111.6-112.0	61.27	61.21	3.44	3.43
NH ₂ ^e	2479-46-1	..	63	114.6-115.1	74.24	74.10	5.52	5.34

^a All melting points are corrected. ^b Lit.⁴ mp 88-89°. ^c Bp 191-193 (0.5 mm). ^d Bp 172-178 (0.5 mm). ^e Prepared by quantitative hydrogenation of the p-nitro analog, using PtO₂ in ethanol.

an example, there should be some dissociation to partially coordinated copper. The incompletely coordinated copper might then catalyze the reaction by acting as a Lewis acid. To test for the necessity of some dissociation of the copper-solvent complex, a reaction was carried out in a mixed solvent consisting of 91% pyridine and 9% 2,2'-bipyridine (eq 2). Except for the



addition of the 2,2'-bipyridine, reaction conditions were as described in method A for the ether condensation in pyridine. The greater complexing by the diamine lowered the yield of *m*-diphenoxybenzene from 70 to 31% in 9 hr. It thus appears that there is an optimum degree of complexing and that the solvent should be regarded as a cocatalyst.

Disodium resorcinate has a low solubility in most organic solvents. Even for the successful solvents shown in Table I, only a small fraction of the disodium resorcinate reactant is in solution at any instant. The reaction requires dissolved phenoxide anions and the best solvents have high dielectric constants. However, the order of effectiveness for solvents cannot be predicted from dielectric constants because of the reactions which occur between solvent and catalyst or reactant.

Acidic solvents destroy phenoxide ions. Water also interferes seriously with the ether condensation. Even 2% water in pyridine retards the desired reaction greatly. Although water can hydrolyze phenolic salts, hydrolysis would not be able to deplete the resorcinate ion concentration seriously in the presence of a large excess of pyridine. However, hydroxyl ion would be formed in this hydrolysis and by reaction between water and pyridine (eq 3). Excess base, added as sodium hy-



droxide or methoxide, completely inhibits the ether condensation by deactivating the catalyst. Retardation by water appears to come about in the same way.

It is evident that solvents may fail to promote the ether condensation for various reasons, sometimes in combination. For example, *n*-decane dissolved neither disodium resorcinate nor cuprous chloride and the reac-

tion failed. On the other hand, 1-butanol and 1-hexanol dissolved both disodium resorcinate and cupric chloride, but they allowed no formation of *m*-diphenoxybenzene and only a 3% yield of *m*-phenoxyphenol. Removal of resorcinate dianion can occur by alcoholysis, along with deactivation of the catalyst by alkoxide ion thus formed.

Other solvents were tested which probably represent classes of compounds unsuitable as catalytic solvents for the ether condensation. These include ethylene glycol, methyl *n*-decanoate, acetylacetone, heptanone-4, diphenyl ether, and bromobenzene. Neither *m*-diphenoxybenzene nor *m*-phenoxyphenol was obtained when these solvents were employed.

Substituted Diphenoxybenzenes.—Various substituted *m*-diphenoxybenzenes were prepared from resorcinol. These products were synthesized by using the appropriately substituted bromobenzenes in method A. The reactions were followed by gas chromatography and terminated when product yields ceased to increase. Yields shown in Table II are based on isolated pure products.

The chloro group is less reactive than the bromo group in the ether synthesis.⁶ Here, only chloro substituents were found on the *m*-diphenoxybenzenes when *p*-chlorobromobenzene was condensed with resorcinol. Acidic substituents cannot be present since they react with the sodium salt of the phenol to destroy phenoxide ions. Both *p*-bromoaniline and *p*-bromo-*N,N*-dimethylaniline failed to react in 6 hr. These amines remained in the worked up reaction mixture. The substituted anilines may have deactivated the catalyst. However, *m*-bis(*p*-aminophenoxy)benzene was readily prepared in quantitative yield from the corresponding nitro compound by catalytic hydrogenation.

Influence of Substituents.—The rate of ether formation depends upon the aryl bromide concentration and, at low copper levels, upon the catalyst concentration. Under our experimental conditions, the disodium resorcinate concentration is fixed by the low solubility of this salt in pyridine. The concentration of disodium resorcinate was then taken as constant during the period of rate measurements. Reactions were carried out as in method A, following the reaction rates by examination of aliquots by gas chromatography. At 1.5 g of cuprous chloride/100 ml of pyridine, the catalyst concentration is threefold above the level at which the rate is influenced by catalyst concentration.

(6) H. Weingarten, *J. Org. Chem.*, **29**, 977 (1964).

AUGUST 1967

SOLVENT-ASSISTED ULLMANN ETHER SYNTHESIS

2503

 TABLE III
 AROMATIC ETHERS BY CONDENSATION OF DISODIUM SALTS OF PHENOLS WITH BROMOBENZENE

Phenolic reactant	Method	Yield, ^a %	Mp, ^b °C	Carbon, %		Hydrogen, %	
				Calcd	Found	Calcd	Found
Hydroquinone	B	0.3 ^a	75.1–78.1 ^d
Catechol	B	3 ^a	90.3–91.3 ^f
4,4'-Isopropylidenediphenol	A	46	58.9–60.3	85.23	84.97	6.38	6.27
2,7-Dihydroxynaphthalene	A	46 ^a	103.7–104.7	84.59	83.88	5.18	5.18
Phloroglucinol	A	0.5 ^a	109.7–110.1 ^f

^a All yields are based on the phenolic reactant. ^b All melting points are corrected. ^c Gas chromatography showed this to be accompanied by a 3% yield of *p*-phenoxyphenol. ^d Lit. mp 74–75°, C. Hausermann and A. Müller, *Ber.*, 34, 1071 (1901); lit.^e mp 77° for *p*-diphenoxybenzene. ^e An 8.6% yield of purified *o*-phenoxyphenol was also isolated. ^f Lit.^g mp 93° for *o*-diphenoxybenzene. ^g Only tars resulted from attempts to condense 1,5-, 1,7-, and 2,6-dihydroxynaphthalenes. ^h The trisodium salt of this trihydric phenol was used. ⁱ Lit.^h mp 110° for 1,3,5-triphenoxybenzene.

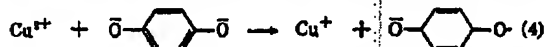
Rate of ether formation then becomes dependent upon only the aryl bromide concentration and the following equation applies.

$$k = \frac{2.303}{t} \log \frac{c_1}{c}$$

Concentration of aryl bromide (*c*) was chosen where the yield of substituted *m*-diphenoxybenzene was 10%, based on the aryl bromide. Thus $\log c/c_1$ is made constant and measurement of the corresponding reaction time (*t*) allows calculation of $\log k/k_0$ for a Hammett ρ constant plot (Figure 1). Rate enhancement by electron-withdrawing substituents is evident, the value of ρ being +1.4. These results indicate nucleophilic attack by resorcinolate dianion.

Aryl iodides would be expected to give faster reaction rates than the corresponding bromides. However, when iodobenzene was used in place of bromobenzene under the conditions of method A, only an 11% yield of *m*-diphenoxybenzene resulted, accompanied by a 7% yield of *m*-phenoxyphenol. Iodide ion is an effective agent for converting cupric copper to cuprous iodide, which is a poor catalyst. Under the conditions of method A, cuprous iodide replacing cuprous chloride on a mole basis allowed only a 1.5% yield of *m*-diphenoxybenzene and a 4.1% yield of *m*-phenoxyphenol.

Catalysis by Copper Salts.—Salts of cuprous and cupric copper, as introduced into the reaction mixture, are about equally effective in catalyzing the condensation of aryl bromides with salts of dihydric phenols. For example, the substitution of cupric chloride for an equimolar amount of cuprous chloride in the preparation of *m*-diphenoxybenzene by method A still gave a 60% yield of that compound. The nonspecificity indicates that the active catalyst may be formed by either oxidation or reduction. For monohydric phenols, Weingarten⁷ concluded that cuprous copper results from the reduction by phenoxide anion, which is thus oxidized to a semiquinone radical. Reduction of copper would proceed readily with resorcinolate dianion and the dianions from catechol or hydroquinone would oxidize even more rapidly (eq 4). Oxidation by cupric



ion can account for the low yields obtained from catechol, hydroquinone, 2,6-dihydroxynaphthalene, 1,5-dihydroxynaphthalene, and phloroglucinol (Table III). These reactions also gave larger yields of tars than the less readily oxidized resorcinol, 2,7-dihydroxynaphtha-

(7) H. Weingarten, *J. Org. Chem.*, 29, 3624 (1964).

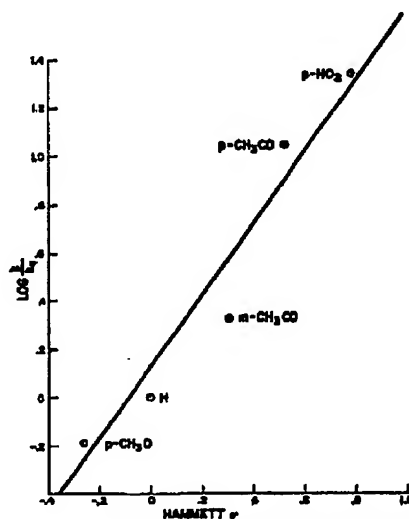
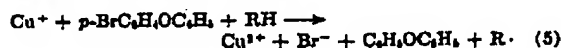


Figure 1.—Hammett plot for substituted bromobenzenes.

lene, and 4,4'-isopropylidenediphenol. Analyses of reaction mixtures by gas chromatography showed that the dihydric phenols were the source of the tars. Polymerizations involving radical ions appear likely.

Under our reaction conditions, aryl bromides are in part debrominated to the corresponding hydrocarbon by cuprous chloride, the copper thus being oxidized to the cupric level. In the case of *p*-bromophenyl phenyl ether (where the debrominated product was isolated from the reaction mixture), the conditions of method A gave a yield of diphenyl ether which was 20% of theoretical based on cuprous chloride (eq 5).



Bacon and Hill⁸ demonstrated a similar debromination of 1-bromonaphthalene by cuprous acetate in pyridine. It thus appeared that under our reaction conditions cupric copper could not be ruled out as catalyst on the basis of its absence from the system. If copper could be held at the cupric level by the addition of an oxidizing agent to the system, the effects of cupric copper could be measured directly, but this is not feasible since the phenols are themselves easily oxidized. Maintaining copper at the cuprous level by means of a reducing agent appeared more attractive,

(8) R. G. R. Bacon and H. A. O. Hill, *J. Chem. Soc.*, 1112 (1964).

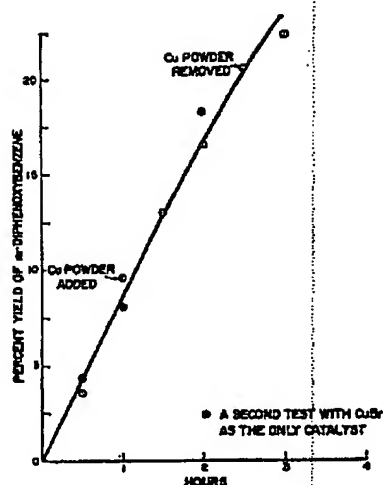


Figure 2.—Test for effect of copper powder on cuprous bromide catalyst.

but any reducing agent which may convert copper ions to copper metal or an inactive salt or complex is unsuitable.

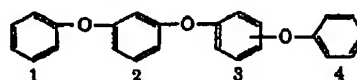
By observing the green cupric bromide-pyridine complex change to the yellow cuprous complex, we found in a preliminary test that a suspension of precipitated copper powder (1.5 g) reduced the copper of cupric bromide (0.55 g) in 100 ml of refluxing pyridine in less than 1 min. We also found that precipitated copper powder does not itself catalyze the ether condensation. To avoid the complications of a heterogeneous reaction system, tests were made upon the sodium salt of *m*-phenoxyphenol which was completely dissolved in pyridine. Precautions described in method A were observed. The reaction employed 2.08 g (0.01 mole) of the sodium salt of *m*-phenoxyphenol in 100 ml of pyridine, 10 g (0.0636 mole) of bromobenzene, and 0.35 g of cuprous bromide catalyst. After the reaction had progressed for 1 hr, there was added 1.5 g of copper powder, freshly precipitated by zinc dust and washed with acetone. When this had been present for 1.5 hr, the copper was filtered out under nitrogen through a fine fritted-glass disk and the reaction was continued for 1 additional hr. The formation of *m*-diphenoxybenzene was followed by withdrawing aliquots at 0.5-hr intervals for analysis by gas chromatography. The presence of the suspended copper powder did not change the reaction rate relative to the initial rate (Figure 2). There was also close agreement with a control run having no added copper metal. If the reaction mixture had to oxidize the cuprous copper to the cupric level to obtain the active form of the catalyst, the reaction should be much slowed down when copper powder reduces cupric copper back to the cuprous level. Absence of a decrease in reaction rate by the reduction of cupric to cuprous copper is evidence for catalysis by cuprous copper.

Nonlinear Polyphenyl Ethers.—The numerous polyphenyl ethers known are based upon linear chains of phenoxy groups except for 1,3,5-triphenoxybenzene, which has been prepared from 1,3,5-tribromobenzene.⁹

(9) F. Ullmann and P. Sponagel, *Ber.*, **28**, 2212 (1905).

Our reaction of bromobenzene with phloroglucinol, under conditions adequate for resorcinol, gave only a trace of 1,3,5-triphenoxybenzene, but the isomeric 1,2,4-triphenoxybenzene and other nonlinear polyphenyl ethers can be prepared indirectly from *m*-diphenoxybenzene.

When *m*-diphenoxybenzene is brominated under mild conditions, 2,4-diphenoxybromobenzene can be obtained in quantitative yield by method D. To prove the structure of the product, the bromo compound was converted to a four-ring ether by reaction with sodium phenoxide in pyridine by method E. This product melted at 59.9–60.4°. The linear four-ring ethers having a *meta*-substituted benzene ring (number 2) have melting points of 40° when ring number 3 is *meta* substituted, 48° when *para* substituted, and 74° when *ortho* substituted by ring number 4.² Thus, the



four-ring ether product must be a triphenoxybenzene and the bromine atom must have gone onto the middle ring of *m*-diphenoxybenzene. Of the three isomers which can be written, 3,5-diphenoxybromobenzene must be excluded since the corresponding 1,3,5-triphenoxybenzene has a melting point of 110°.⁹

Selection between the two remaining bromides was made on the basis of the nuclear magnetic resonance spectrum. 2,6-Diphenoxybromobenzene has no hydrogen atoms to be shifted downfield by an *o*-bromine atom, whereas 2,4-diphenoxybromobenzene has such a hydrogen atom. The downfield shift of this hydrogen atom was observed and all three hydrogen atoms on the middle ring were accounted for. Further, the spectrum of this product could not have been generated by the symmetrical isomers, 2,6-diphenoxybromobenzene and 3,5-diphenoxybromobenzene.

Experimental Section

Melting points are all corrected. A Fisher Scientific Co. melting point block, calibrated by eight standards in the range of interest (40–140°), was used. Samples were held between cover slips while the temperature was raised 1 deg/min. Boiling points are not corrected.

Method A. *m*-Diphenoxybenzene.—A suspension of 10.6 g (0.196 mole) of sodium methoxide in 200 ml of benzene was prepared by stirring under a pure nitrogen stream in a 500-ml flask. The flask was also fitted with a stirrer, a dropping funnel, and a condenser arranged for distillation. All reactions in the flask were carried out under nitrogen. Then 11.0 g (0.100 mole) of resorcinol was added. Benzene and methanol were distilled off to leave a white powder of the resorcinol salt. When the salt had cooled, the condenser was arranged for reflux. Then 200 ml of pyridine was added. The stirred mixture was brought to reflux and 42 ml (0.40 mole) of bromobenzene was added rapidly through the dropping funnel. This was followed at once by the addition of 3.0 g of cuprous chloride. The reaction mixture was brought back to reflux and held at reflux for 9 hr under a blanket of nitrogen. The reaction mixture was then poured into 600 ml of water and hydrochloric acid was added until acidified. The product was extracted into four 200-ml portions of *n*-pentane and the pentane solution filtered. *n*-Pentane was removed by distillation. Distillation at 0.1 mm removed bromobenzene from the residue. The crude product crystallized on cooling. Recrystallization from 95% ethanol gave 18.4 g (70%) of *m*-diphenoxybenzene, mp 59.9–60.4° (lit.² mp 59.5–60.0°). Mixture with an authentic sample (mp 60.2–60.6°) from Distillation Products Industries did not depress the melting point.

AUGUST 1967

SOLVENT-ASSISTED ULLMANN ETHER SYNTHESIS

2505

Anal. Calcd for $C_{13}H_{11}O_2$: C, 82.42; H, 5.38. Found: C, 82.29; H, 5.58.

Method B. *o*-Phenoxyphenol.—Sodium hydride, 4.57 g (0.19 mole), was added as a *n*-pentane dispersion to 100 ml of methyl sulfoxide. The addition was carried out in a 500-ml flask under a nitrogen stream. The mixture was heated to 60° until the evolution of hydrogen ceased; then 11.0 g (0.100 mole) of catechol was added in solution in 100 ml of methyl sulfoxide. During all operations, the reaction mixture was protected by a stream of nitrogen. The temperature was brought up to 150° and *n*-pentane distilled out. The condenser was arranged for reflux and stirring was continued. Then 42 ml of bromobenzene (0.40 mole) was added in a stream through a dropping funnel. This was followed by the addition of 5.0 g of cuprous chloride. The reaction mixture was brought back to 150° and held at this temperature with stirring under a nitrogen blanket for 19 hr. It was then poured into 500 ml of water containing 10 ml of hydrochloric acid. The organic layer was extracted by two 200-ml portions of benzene. To the combined benzene extracts there was added 2 l. of *n*-pentane. The tar thus precipitated was filtered off. The pentane layer was extracted with three 100-ml portions of 5% aqueous sodium hydroxide solution. Acidification by hydrochloric acid yielded *o*-phenoxyphenol, which was extracted into *n*-pentane. Evaporation of the pentane gave 3.03 g of crude product. Recrystallization from 95% ethanol yielded 1.60 g (8.6%) of *o*-phenoxyphenol, mp 104.7–104.9° (lit.¹⁰ mp 105–106°).

Anal. Calcd for $C_{12}H_9O_2$: C, 77.40; H, 5.41. Found: C, 77.08; H, 5.39.

Method C. *m*-Phenoxyphenol.—The reaction flask was blanketed with nitrogen and 750 ml of dry pyridine was introduced. Resorcinol, 495 g (4.5 moles), was dissolved in the pyridine with stirring. Then 162 g (8.0 moles) of sodium methoxide was added. The mixture was stirred and methanol was fractionally distilled from the mixture over a period of 0.5 hr. Bromobenzene, 1420 g (9.00 moles), was run into the reaction flask. This was followed by 22 g of cuprous chloride. The mixture was refluxed, with stirring under nitrogen for 3 hr. Pyridine was then distilled off while the pot temperature rose to 150°. The residue was poured into a solution of 500 ml of concentrated hydrochloric acid in 1100 ml of water and stirred. The organic layer was dissolved in 1 l. of benzene. This benzene solution was washed with 100 ml of hydrochloric acid in 100 ml of water. The benzene solution was then extracted by 100 g of sodium hydroxide in 1 l. of water. This was followed by a second extraction by 20 g of sodium hydroxide in 200 ml of water. The combined alkali extracts were acidified by concentrated hydrochloric acid. Liberated *m*-phenoxyphenol was extracted into 300 ml of benzene. Benzene was removed by distillation at atmospheric pressure. Distillation was continued at 0.8 mm to yield 350 g (42%) of *m*-phenoxyphenol distilling at 158–165° (lit.⁴ bp 143–148° (2 mm)). Gas chromatography indicated 99+ % purity.

Anal. Calcd for $C_{12}H_9O_2$: C, 77.40; H, 5.41. Found: C, 77.50; H, 5.40.

Method D. 2,4-Diphenoxybromobenzene.—A solution of 100 g (0.725 mole) of *m*-diphenoxybenzene was prepared by stirring with 400 ml of benzene at room temperature in a 2-l. flask fitted with a reflux condenser and dropping funnel. Stirring was continued and a solution of 118 g (0.725 mole) of bromine in 400 ml of benzene was dropped in slowly over a period of 3 hr. The mixture was then allowed to stand overnight (17 hr). Benzene and hydrogen bromide were distilled from the mixture. The last of the benzene was removed in a stream of nitrogen until the flask came to constant weight; the yield of 2,4-diphenoxybromobenzene was 247 g (100%); gas chromatography indicated 99% purity; the boiling point was 167–169° (0.4 mm).

(10) J. F. Norris, B. G. Macintyre, and W. M. Corne, *Am. Chem. J.*, **29**, 197 (1903).

Anal. Calcd for $C_{19}H_{15}BrO_2$: C, 63.36; H, 3.84; Br, 28.4. Found: C, 63.48; H, 3.98; Br, 23.1.

Method E. 1-(*m*-Phenoxyphenoxy)-2,4-diphenoxybenzene.—A 500-ml flask was fitted with a nitrogen inlet tube, a 1-ft-long Vigreux column, and a stirrer to prepare a solution of 55.8 g (0.300 mole) of *m*-phenoxyphenol in 200 ml of pyridine at room temperature under nitrogen. Stirring was continued while 15.6 g (0.288 mole) of sodium methoxide was added. Then 135 ml of methanol-pyridine mixture was distilled out through the column over a 1-hr period. After cooling, the column was replaced by a reflux condenser. Then 67.9 g (0.189 mole) of 2,4-diphenoxybromobenzene was added. This was followed by 2 g of cuprous chloride, washed in by 25 ml of pyridine. The mixture was refluxed with stirring for 4 hr. Pyridine was then distilled out until the pot temperature reached 160°. The reaction mixture was poured into a solution of 50 ml of hydrochloric acid in 500 ml of water and allowed to stand overnight. After decanting off the aqueous layer, the crude product was dissolved in 430 ml of benzene. This benzene solution was washed by 20 ml of hydrochloric acid in 200 ml of water and again by 10 ml of hydrochloric acid in 100 ml of water. Unreacted *m*-phenoxyphenol was extracted into 12 g of sodium hydroxide in 150 ml of water, used in two equal portions. The benzene solution was then washed with 100 ml of water. Benzene was removed by distillation. Distillation was continued at 0.5 mm to give a product collected over the range 262–268°; the yield of 1-(*m*-phenoxyphenoxy)-2,4-diphenoxybenzene was 35.8 g (40%); gas chromatography indicated 99+ % purity.

Anal. Calcd for $C_{26}H_{21}O_3$: C, 80.69; H, 5.06. Found: C, 80.66; H, 4.97.

1,2,4-Triphenoxybenzene was obtained in 42% yield from 2,4-diphenoxybromobenzene reaction with sodium phenoxide by method E, mp 59.9–60.4°.

Anal. Calcd for $C_{26}H_{21}O_3$: C, 81.28; H, 5.13. Found: C, 81.25; H, 5.21.

m-Bis(2,4-diphenoxyphenoxy)benzene was obtained in 12% yield from 2,4-diphenoxybromobenzene reaction with disodium resorcinate by method E, mp 109–111°.

Anal. Calcd for $C_{32}H_{25}O_4$: C, 79.99; H, 4.79. Found: C, 79.23; H, 4.81.

Materials.—Solvents were dried for at least 48 hr over Linde Molecular Sieve 4A. Phloroglucinol was dehydrated by a toluene distillation. Other materials were used as received from the suppliers. Resorcinol, hydroquinone, catechol, phloroglucinol, bromobenzene, iodobenzene, *p*-bromotoluene, *p*-bromoanisole 4'-bromoacetophenone, 1-bromo-4-chlorobenzene, sodium methoxide, methyl sulfoxide, 2,2'-bipyridine, and cuprous oxide were purchased from Matheson Coleman and Bell Division of the Matheson Co; 2,7-dihydroxynaphthalene, *p*-bromophenyl phenyl ether, and 1-bromo-4-nitrobenzene were from Distillation Products Industries; pyridine, cuprous chloride, and cupric bromide were from J. T. Baker Chemical Co.; cuprous bromide and cuprous iodide were from Fisher Scientific Co.; cupric chloride was from Baker and Adamson; sodium hydride was from K & K Laboratories; and 4,4'-isopropylidenediphenol was from Union Carbide Chemicals Co.

Registry No.—*m*-Diphenoxybenzene, 3379-38-2; *o*-phenoxyphenol, 2417-10-9; *m*-phenoxyphenol, 713-68-8; 2,4-diphenoxybromobenzene, 13118-87-1; 1-(*m*-phenoxyphenoxy)-2,4-diphenoxybenzene, 13118-88-2; 1,2,4-triphenoxybenzene, 13118-89-3; *m*-bis(2,4-diphenoxyphenoxy)benzene, 13118-90-6.

Acknowledgment.—The authors wish to thank Dr. John C. Ballar, Jr., and Dr. Glen A. Russell for helpful discussions during the course of this work.

**This Page is Inserted by IFW Indexing and Scanning
Operations and is not part of the Official Record**

BEST AVAILABLE IMAGES

Defective images within this document are accurate representations of the original documents submitted by the applicant.

Defects in the images include but are not limited to the items checked:

- ☐ BLACK BORDERS
- ☐ IMAGE CUT OFF AT TOP, BOTTOM OR SIDES
- ☐ FADED TEXT OR DRAWING
- ☐ BLURRED OR ILLEGIBLE TEXT OR DRAWING
- ☐ SKEWED/SLANTED IMAGES
- ☐ COLOR OR BLACK AND WHITE PHOTOGRAPHS
- ☐ GRAY SCALE DOCUMENTS
- ☒ LINES OR MARKS ON ORIGINAL DOCUMENT
- ☐ REFERENCE(S) OR EXHIBIT(S) SUBMITTED ARE POOR QUALITY
- ☐ OTHER: _____

IMAGES ARE BEST AVAILABLE COPY.

As rescanning these documents will not correct the image problems checked, please do not report these problems to the IFW Image Problem Mailbox.